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PROGRESS IN NANOSTRUCTURED PHOTOELECTROCHEMICAL SOLAR CELLS

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ABSTRACT

The paper deals with basic processes involved in light capture and electron transport through a photoelectrochemical cell consisting of a dye absorber and semiconductor-electrolyte electron transport systems. The use of quantum chemical calculations to characterise and optimise the choice of materials is illustrated by *ab initio* treatment of a promising organic dye, which in a PEC cell is attached to a nanostructured anatase semiconductor and interacts with iodine redox couples in conventional electrolytes. Progress in understanding the ultra-fast electron transfer between dye and semiconductor surface is presented, as well as preliminary calculations on the effect of the dye molecule being imbedded into a solution.

1. INTRODUCTION

Creating an optimised design of a photoelectrochemical (PEC) solar cell requires control over a succession of processes: light absorption by the sensitiser dye, electron transfer between dye and semiconductor, transport of electrons between nanostructured semiconductor nodules to the anode conductor, electron transfer between electrolyte and dye, redox shuttle function and transport, and cathodic removal of electron from cathode to electrolyte. Some of these processes are well known from battery and fuel cell technologies, and need only to be adjusted to the particular materials used in the PEC solar cell. Others are novel and specific to PEC devices, such as the excitation of and transfer to and from the dye molecules. These are the primary aim of the modelling efforts described in this paper. The transport through the nanostructured semiconductor material is in principle also a complex phenomenon, but simple models have been shown to work well for this type of transport, provided that the formation of the nanostructured semiconductor is done in such a way that nodule contact is ensured. The optical path of light through the nanostructured material to the final absorption in the dye monolayers residing on the nodule surfaces is also a phenomenon amenable to conventional modelling, although methods from classical optics have to be supplemented by quantum theory.

The paper concentrates on the progress in quantum calculations of dye excitation, adding to the discussion made in a recent survey paper [1]. The specific dye selected for the calculations is a coumarin-derivative [2] shown in Fig. 1, typical of a family of structures recently synthesised [3]. The overall design of a PEC cell with indication of the placement of the dye upon a nanostructured semiconductor surface is shown schematically in Fig. 2.

2. COUMARIN-DERIVATIVE STRUCTURE

The selection of a suitable sensitiser for a PEC cell is made on the basis of a number of requirements including

- high absorption capability over the range of spectral frequencies characteristic of sunlight
- energetically suitable excited states
- good attachment to semiconductor nanoparticles, that ensures rapid electron transfer (in competition with de-excitation and back-transfer from semiconductor surface to dye sensitiser)
- easily accepting replacement electron from electrolyte
- dye lifetime consistent with stipulated device life

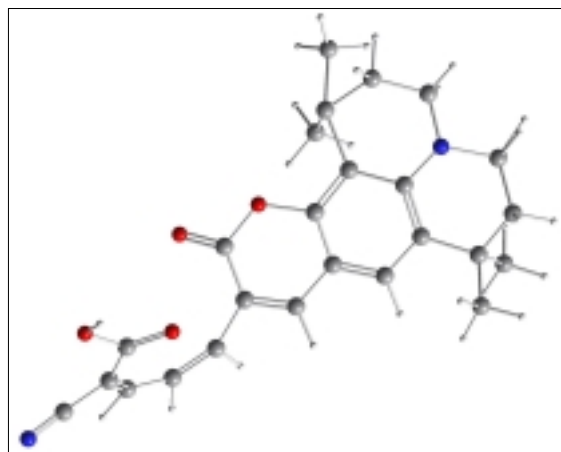


Fig. 1. Optimised structure of coumarin-derivative organic dye synthesised by [3] (this and following Figs. are reproduced with permission from [1] or [4])

The search for optimised sensitisers have usually focussed on a particular family of molecules. For example, the Grätzel/Lausanne group has looked at metal complexes, notably based on ruthenium polypyridines, meticulously synthesising one variant after the other, adding rings, thiocyanate ligands and carboxylate groups in different combinations. The size of the molecule, in combination with its excitation spectrum, determines the frequencies of solar radiation that can be absorbed, and the associated cross sections. The "black dye" (Ru, 3 pyridine rings, 3 thiocyanate ligands and 3 carboxylate groups) has led to the highest overall conversion efficiency, being 10% for laboratory cells (area about 10^{-4} m²) [12]. For comparison, an efficiency of 5% is claimed for a large cell (of the order of 1 m²) in industrial production [13].

Fig. 1 shows the optimised shape of a coumarin-derivative dye proposed by the Arakawa-group [3], Fig. 2

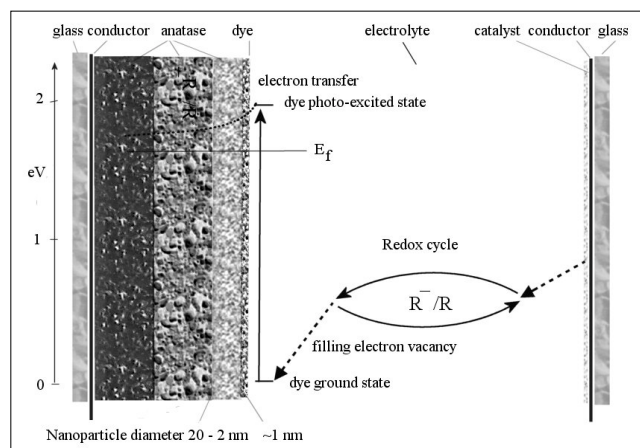


Fig. 2. Layout of PEC solar cell with indication of energy levels (E_f is the Fermi level of the semi-conductor material)

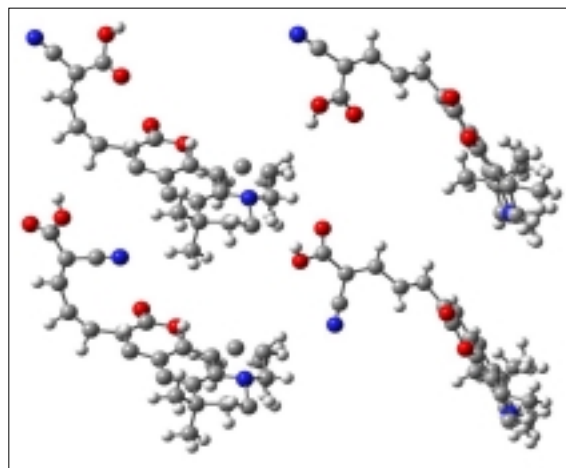


Fig. 3. Shape isomers of coumarin-derivative dye.

shows the entire PEC cells with the position of the sensitizer dye, and Fig. 3 some shape isomers identified, the top left being slightly lower in energy [1].

The optimisation calculations was using a simple set of 331 basis states (3-21G), while the final calculations of the excited state through which transfer to the anatase surface is passing, used a larger basis set of 838 basis functions, including diffuse polarization functions (6-311+G(d,p)) [5]. The Schrödinger equation is solved under the assumptions:

- nuclear motion neglected
- Gaussian functions are used as basis: they are linear combinations of atomic wave functions
- the Hartree-Fock method is used to find a selfconsistent solution in terms of determinants of a set of "molecular orbitals" (MO), which again are linear combinations of the Gaussian functions with coefficients to be determined.
- Hartree-Fock (HF) implies that each electron is moving in the mean field from all the other particles. This allows the best ground state wave function to be determined.
- higher electron correlations are added as needed, in order to get better predictions for energies, and to determine excited states, the calculation of which by time-

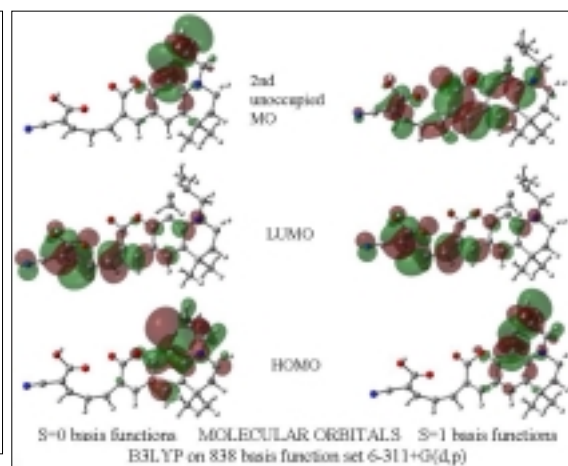


Fig. 4. Electron density of HOMO, LUMO and 2nd excited molecular orbital, based on selfconsistent field (SCF) calculations including electron correlations of the B3LYP form in a basis of 838 wave functions. The column to the right (left) uses triplet (singlet) base functions.

dependent HF involves determining the lowest eigenvalues of a determinant. This can be carried to any order, approaching the exact solution to the Schrödinger equation.

Fig. 4 shows the molecular orbits near the Fermi level for the selfconsistent ground state calculation including higher electron correlations. It is seen that moving an electron from the highest occupied orbit (HOMO) to the lowest unoccupied one (LUMO) involves reducing the electron density in the coumarin-part of the molecule, and increasing it along and particularly at the end of the "arm" attached to the molecule. If the electron correlations had not been included, the energy difference LUMO minus HOMO would be nearly 8 eV, as opposed to an experimental value of 1.8 eV [15]. By including correlations, the energy comes down to the experimental value or lower, as shown in Fig. 5. The second unoccupied orbit shown in Fig. 4 is quite different in nature.

The observed 1st excited state is likely an S=1 state, which explains why the calculation with S=1 basis states does better. For an S=0 Hartree-Fock calculations, such as the one giving the best ground state energy, one can also calculate S=1 excited states, but it is a common feature that they are less reliable than the excited states obtained from a time-dependent Hartree-Fock calculation using "artificial" S=1 molecular orbitals such as the ones shown in Fig. 4.

A range of different approximations successively applied to the calculation of coumarin-derivative excited states are summarised in Fig. 5. The first column shows the molecular orbit energy difference from a pure HF calculation without further correlations.

A first orientation on the correlations may be obtained from simple semi-empirical methods like ZINDO-1 [6], shown in column 2 of Fig. 5. A basis of 10 molecular orbitals on each side of the Fermi level has been included. This gives a lowest excited triplet (spin=1) state at 1.40 eV and a second singlet (spin=0) state at 1.95 eV.

As the next step, one may use the *ab initio* ground state calculation and add various types of configuration

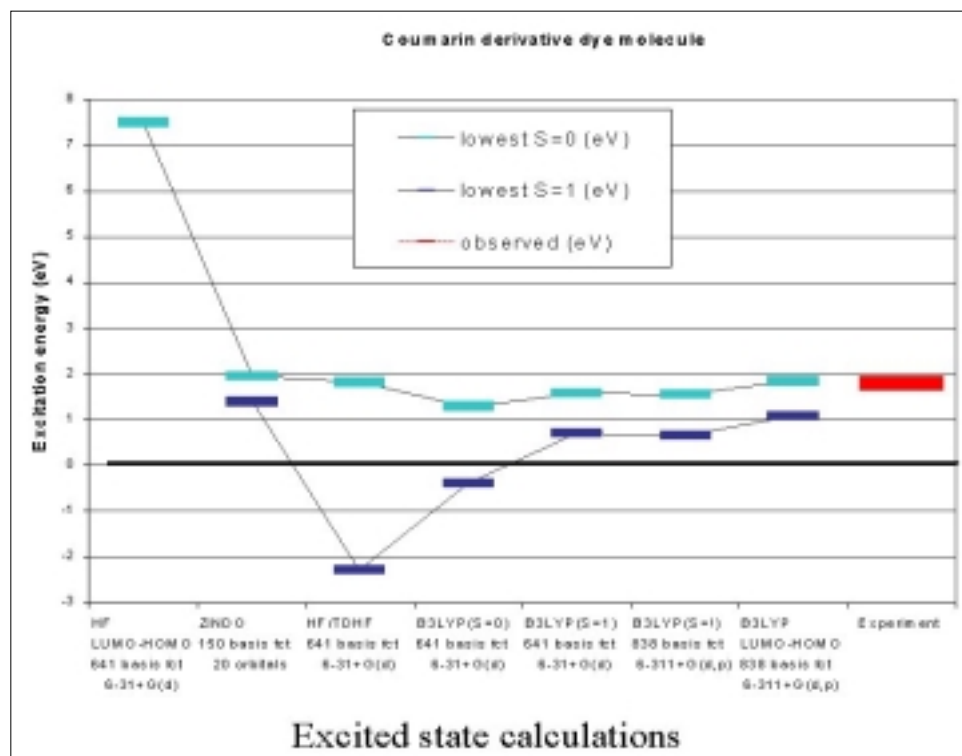


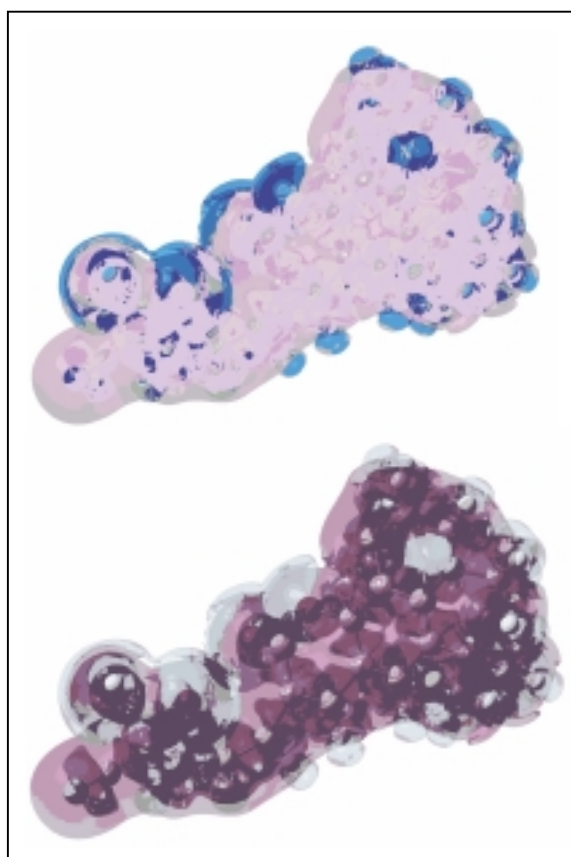
Fig. 5 (left). Summary of excited state calculations for a coumarin-derivative dye molecule. The lighter bars above are S=0 states, the lower solid bars are S=1. See text for discussion.

Fig. 6 (below). Calculated electron density difference between first excited singlet and ground state of coumarin derivative dye (bottom: negative values enhanced, top: positive values enhanced).

interaction. The ground state is first calculated with an enlarged basis of 641 base functions forming 1096 gaussian functions, including polarisation and diffuse functions [4]. In the HF calculation, this lowers the ground state energy by some 215 eV. A further improvement is including some lower order of configuration interaction in the energy calculation, by a density functional method [7] including exchange forces, as proposed by Becke and denoted B3LYP [8]. This brings the ground state energy down by a further 225 eV.

As regards the first excited state, the high degree of correlation indicated by the semi-empirical calculation (or by the difference between the 8 eV uncorrelated MO difference and the observed 1.8eV excitation) makes it difficult to succeed with a simple calculation. Linear combinations of excitation of single electrons between MO's (called CIS) failed to converge, and a time-dependent Hartree-Fock (TD) [9,10] solution contains spurious states, which however moves rapidly up in energy, as the ground state calculation includes more and more correlation (HF to B3LYP). The B3LYP+TDHF calculated with the 641 singlet basis orbits (column 4 in Fig. 5) still have one negative energy, but with the use of spin-1 (triplet) basis states, the excitation energies all become physically acceptable (column 5)

The basis was finally increased to 838 orbits (column 6), and adding polarisation also to hydrogen functions, but this did not change the excitation energies, which are thus believed to be essentially correct for the model. The predicted energies are 0.70 eV (triplet) and 1.3 eV (singlet), followed by another singlet state at 1.44 eV and another triplet at 1.58 eV. It is interesting that despite the obviously unphysical negative excited states in the plain TDHF calculation (column 3), the corresponding wave functions change smoothly across to the presumably correct excited states with proper positive excitation ener-



gies, obtained in the B3LYP case of column 6.

If the molecular orbitals are evaluated on the basis of the interacting wave functions, they become more correlated and have smaller LUMO-HOMO energies than those obtained from the HF ground state calculation. For

example, the B3LYP LUMO-HOMO energy is 1.8 eV (down from the 8 eV in HF). On the other hand, the expansion of excited states on the more correlated MO basis tend to have fewer components. This shows that the effect of truncating the configuration space is still felt. As mentioned, the calculation of triplet excited states using a complete active space configuration method [11] does better when started with a basis of orbitals that are all spin=1.

Fig. 6 shows the electron density difference between the first singlet excited state of the coumarin-derivative, and the ground state, using the large basis HF+TD calculation. The excited state comprises 15 significant MO excitation pairs. The density difference shows the expected already surmised from the HF ground state MO's, that the excitation moves electron density from the coumarin core to the peripheral arm added to the molecule. It would then be natural to assume, that this is from where the transfer to the anatase surface, upon which the dye sits, takes place. This interpretation is supported by the large dipole moment found in the calculation (13.7 debyes).

Fig. 7 shows the total ground state energy of the successive approximative calculations discussed above. Like for the excited states, the value stabilises with the B3LYP calculations, and adding basis states and polarised hydrogen functions does not change the energy. Fig. 7 also shows the results of adding the effects of the molecule being in a solution (the acetonitrile electrolyte having a dielectric constant of 35.9), using a simple Onsager reaction field model [11]. The effect is seen to be modest but non-zero.

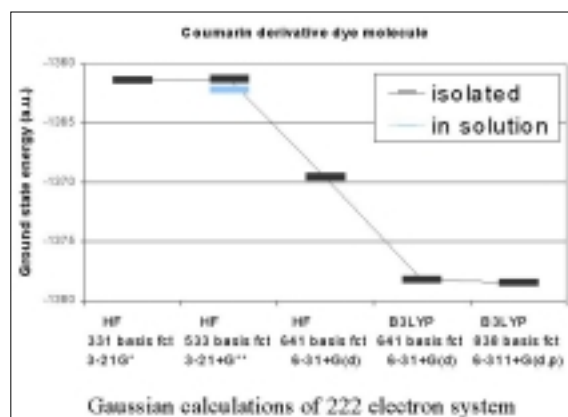


Fig. 7. Successive ground state calculations of increasing complexity, for the coumarin-derivative dye molecule in isolation or imbedded in a solution (grey bar).

3. CONCLUSIONS

The coumarin-derivative organic dye molecule studied is an example of a new family of dyes holding promise for photoelectrochemical solar cells. The structure of the molecule has been determined by an *ab initio* optimisation calculation, and subsequently, more detailed quantum calculations have been made to determine the energies of the ground state and the first excited states. The result is that the excited state likely to play the role of delivering an electron to the anatase surface upon which the dye

molecule sits is an S=1 state of highly collective nature, i.e. involving modifications of the wave functions of a large number of electrons in the molecule. This and the large dipole moment found explains the rapid transfer observed in dye solar cells based on this molecule.

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